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- New low temperature molten salt developed for use as battery electrolyte
- Physical-chemical properties determined
 - phase diagram
 - densities
 - conductivities
 - viscosities
 - structure
 - vapor pressures
 - electrochemical reactions

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Room Temperature Molten Salts for Advanced Energy Conversion and Storage

Very high energy density electrical power sources will be required by the Air Force for operations in space. New high performance electrolytes are being developed to enable a new generation of electrochemical power sources.

by John S. Wilkes

Electrical power is clearly the most versatile form of energy that our civilization uses. It is the "common currency" of the energy economy because it is easy to control and large quantities may be transmitted cheaply over very long distance. It performs useful work at the scale of megawatts, as in Hall cells in aluminum refining, down to nanowatts in an integrated circuit. The feature of electrical power most relevant to this report is the fact that it can be "put in a bottle" and retrieved at the users convenience. The device for such storage is the battery.

Electrochemical power enjoys a favorable location on the power-duration map for power sources. It is clear that in space only nuclear power can provide massive amounts of power for extremely

long periods. The practical and political limitations of nuclear power have prevented its widespread use for space applications (at least in US hardware). The two "ears" of electrochemical power along the duration and power axes show that electrochemical devices can provide very high power for short times and low power for long periods (see the figure). This is one reason why electrochemical power devices, batteries and fuel cells, have been the principal electrical power source throughout the history of our manned spaceflight program.

A battery or fuel cell is simply a device that converts the free energy of chemical reactions directly to electrical energy. Electrochemical conversion has a fundamental thermodynamic advantage over other methods in that it avoids the

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"Carnot limitation." This means that since heat is not involved in the electrochemical process, the efficiency is not determined by temperature. Electrochemical devices can, and usually do, operate very efficiently at modest temperatures.

The optimization of an electrochemical power technology is not a one-dimensional problem. One may easily increase the power capacity at the cost of high weight. Energy can be traded-off for safety, and rate can be traded for lifetime. For space power, as well as many terrestrial applications, the single most cited figure of merit is energy density, also known as specific energy. This is the energy available from the device per unit of mass. The units are watt-hours per kilogram (W-hr/kg). One must be careful in interpreting an energy density reported for a particular battery, since actual and theoretical values are much different. The actual energy density uses the measured performance and includes the mass of the entire cell (case, leads, electrolyte, etc.). The theoretical value is calculated from the free energy of the electrochemical reactions divided by the mass of reactants. Theoretical energy densities are useful at the basic research level, since one cannot predict the engineering trade-offs that will occur during the development cycle of a cell. A rule of thumb is that realistic actual energy densities are one-quarter to one third of theoretical.

The mature technology for secondary (rechargeable) batteries in space applications is nickel-cadmium (Ni-cad), which gives 35 W-hr/kg energy density. Nickel-hydrogen technology (Ni-H₂), at 55 W-hr/kg, is the best available technology that is deliverable for spacecraft being launched today. In fact, the Hubble space telescope was the first actual mission for Ni-H₂. The next generation of technology for secondary batteries, sodium-sulfur, has already been chosen by Air Force and NASA planners to replace Ni-H₂. The sodium sulfur technology, with 100 W-hr/kg energy density, is now in the test and evaluation stage of development, but already there is a call for higher performance batteries.

The task of improving performance beyond sodium-sulfur is a formidable one. Since sodium-sulfur has the best performance of all emerging technologies for secondary batteries, a reasonable goal is to improve upon its performance. Specifically, one would like to increase the operating voltage and energy density and decrease the operating temperature. The voltage goal will require reactants more energetic than sodium and sulfur. The energy density goal translates to anodes and cathodes with a theoretical energy density of about 500 W-hr/kg or greater. The temperature requirement means an entirely different electrolyte must be used (the sodium-sulfur battery has a ceramic electrolyte that conducts poorly below 150°C.)

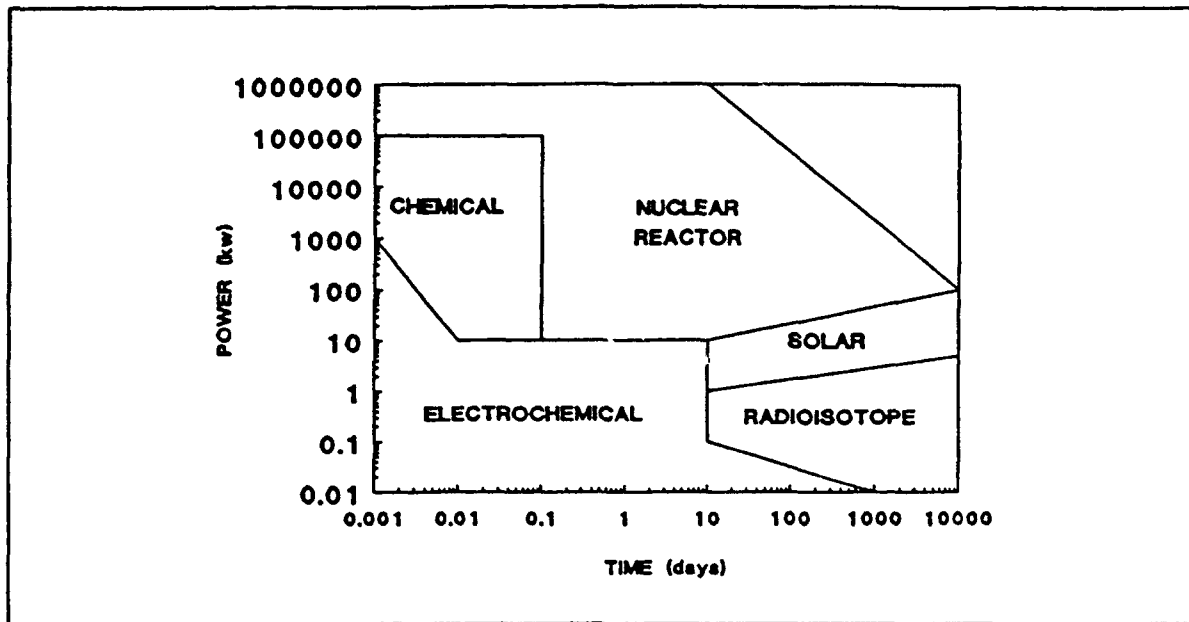
Chemists at FJSRL, in concert with USAF Academy faculty and cadets, are using a three-fold approach to the problem of an advanced high energy secondary battery:

- Obtain an electrolyte with broad liquidus range and wide electrochemical window
- Select energetic and reversible electrochemical reactions
- Demonstrate potential performance of the system as a battery cell

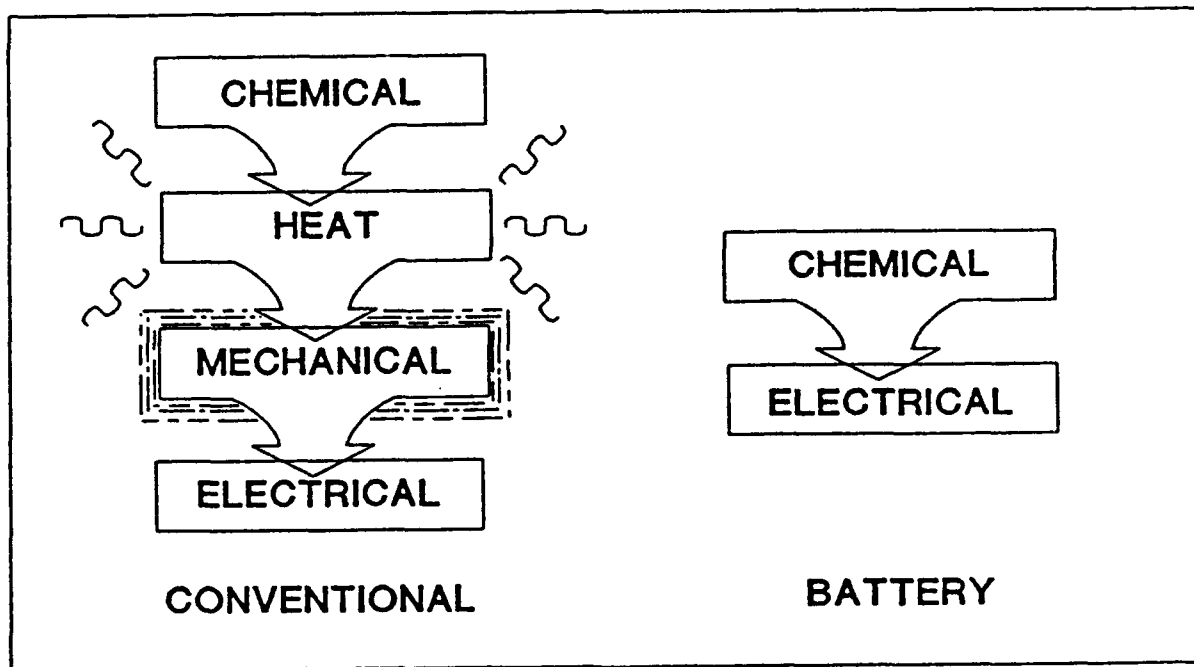
These three steps are not necessarily sequential, and the results from one task will affect the approach of the other two.

The verbs in the approaches are purposefully vague, since each aspect itself requires a variety of intermediate goals and approaches. Taken together, the project uses the skills of analytical, computational, organic, inorganic, and physical chemists as well as electrochemists.

Molten salt electrolytes have been used for many years in some special battery applications, but in all cases they utilize salts with high melting temperatures. In fact, most people would automatically equate *molten* with *hot*. Tactical missiles



The power-duration map for space power sources. The areas included by the boundaries show the regimes where a particular technology is most advantageous. If all other things were equal, then nuclear power would be the technology of choice. The constraints of politics, safety and size for nuclear power make electrochemical devices predominate in the space environment.

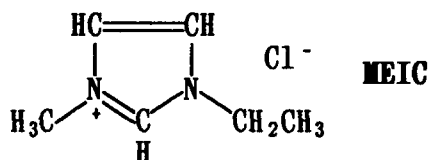


Chemical to electrical energy conversion. The most common method for conversion of energy stored as chemical fuels is to convert the chemical free energy to heat in combustion, convert the heat to mechanical energy in a turbine, and then generate electricity with a mechanical generator. Since heat is involved, high temperature gives better efficiency. In a battery, the free energy of reaction converts directly to electrical energy.

use thermal batteries, which have a KCl-LiCl electrolyte operating at 375°C. This is acceptable for a battery with the short lifetime expected for a missile (less than 30 minutes). In the 1970's, workers at FJSRL proposed and demonstrated an alternative molten salt electrolyte with a substantially lower melting temperature. That material, a mixture of sodium chloride (NaCl) and aluminum chloride (AlCl₃), could operate at 175°C. A battery with the NaCl-AlCl₃ electrolyte was developed by Eureka Corp. and bid (unsuccessfully) for the AMRAAM.

Binary molten salts with AlCl₃ as one component are known as chloroaluminates. It occurred to us that if the NaCl-AlCl₃ mixture could have such a low melting point (its eutectic point is 108°C) perhaps some other related chloroaluminate could be liquid at room temperature. We reasoned that the chloroaluminate melts were low melting because of the large and diverse anions (*vide infra*), so the introduction of a large cation in the place of Na⁺ could reduce the melting points below 100°C. A several year effort that combined theoretical calculations, chemical syntheses and physical properties measurements culminated in the discovery of a new chloroaluminate molten salt with extraordinary properties.

This new material is a mixture of an organic salt, 1-methyl-3-ethylimidazolium chloride, with aluminum chloride that we abbreviate MEIC. Fortunately, a detailed knowledge of the organic salt is not necessary for an understanding of molten-salt batteries. For the record it has the structure:



Actually, the structure of the MEI⁺ cation imparts important structural features to the molten salt, and the physical properties are largely controlled by that structure.

Details of the nature and importance of structure will be left to a later report.

The MEIC-AlCl₃ molten salt is now widely used in the research community, and is finding several industrial uses. The acceptance of the new material is due in large part to our effort to carefully characterize its physical properties. Since it was a new material when we discovered it, one could not look up its properties in the *Handbook of Chemistry and Physics*. Obviously, knowledge of the properties of the electrolyte is essential for its practical use. To date we have measured and reported the following properties:

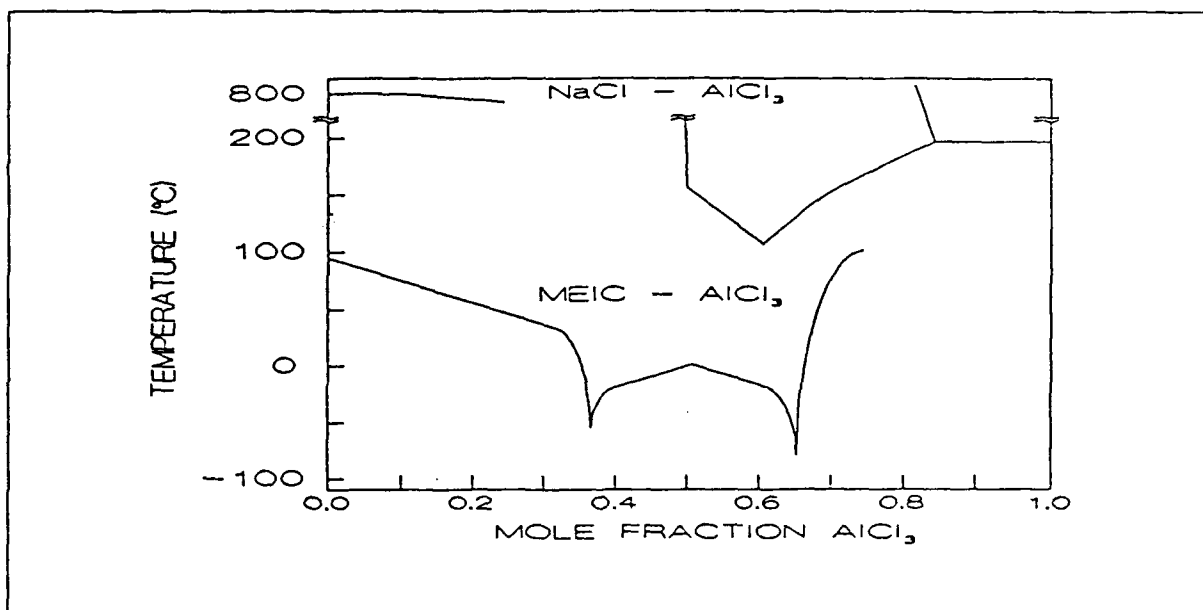
- phase diagram
- electric conductivity
- viscosity
- vapor pressure
- thermal stability
- diamagnetic susceptibility
- gas solubilities

One should realize that each of these properties varies as a function of temperature and the composition of the molten salt, *i.e.* the ratio of MEIC and AlCl₃. A physical property determination is therefore a three-dimensional problem, and thus demanded extraordinary perseverance in the measurements and some creativity in modeling the property in both the temperature and composition space.

Our success in "obtaining" a molten salt with a low melting temperature may be seen in the phase diagram. The liquidus line lies below room temperature over a wide range of compositions, so the material is probably better called a non-aqueous solvent rather than a molten salt. In fact, at some compositions the material remains fluid almost to -100°C. We also know from vapor pressure and thermal stability measurements that the liquid behaves well up to about 250°C. This 350° range is greater than any other electrolyte used in electrochemical devices, and easily covers

Major Secondary Battery Systems

| Battery system | Typical working Voltage, V | Actual energy density W-hr/kg |
|----------------------------|----------------------------|-------------------------------|
| Lead-acid | 2.0 | 35 |
| Nickel-cadmium | 1.2 | 35 |
| Nickel-hydrogen | 1.2 | 55 |
| Sodium-sulfur (high temp.) | 1.7 | 100 |

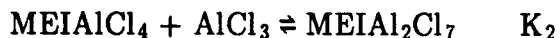


The phase diagram for the MEIC- AlCl_3 binary molten salt. The material is liquid over a wide range of compositions. The two regions at very low temperatures are glass transitions. Some compositions never freeze.

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the MIL-STD specification for battery operations (-40° to $+165^{\circ}\text{F}$).

It is necessary to understand the Lewis acid-base chemistry and anion speciation to appreciate recent developments in the room temperature chloroaluminate electrolytes. The chemical nature of the material is largely governed by the fact that the AlCl_3 is a chloride acceptor (a Lewis acid) and the MEIC is a chloride donor (a Lewis base). A simplified chemical model for the electrolyte is as follows:



MEIC is composed of the ions MEI^+ (structure given earlier) and Cl^- ; MEIAlCl_4 is MEI^+ and AlCl_4^- ions, and $\text{MEIAl}_2\text{Cl}_7$ is MEI^+ and Al_2Cl_7^- ions. AlCl_3 is a non-ionic compound in the liquid and gas state (it is actually the dimer Al_2Cl_6). The values of the equilibrium constants K_1 and K_2 are high, so both of the reactions proceed to completion from right to left. When MEIC is in excess, the melt is termed "basic" and the predominate anions are Cl^- and AlCl_4^- . When AlCl_3 is in excess the melt is termed "acidic" and the predominate anions are AlCl_4^- and Al_2Cl_7^- . When the components MEIC and AlCl_3 are precisely equal, the melt is termed "neutral" and the only anion present is AlCl_4^- .

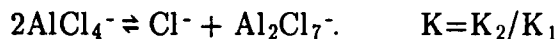
Whether the melt is basic, acidic or neutral has immense electrochemical consequences. The electrochemical window is the range of potentials over which the electrolyte itself is electrochemically inert. A battery cannot have a higher voltage than the breadth of the electrochemical window of the electrolyte. The windows for acidic and basic MEIC- AlCl_3 melts are 2.5V and 2.9V respectively, and the windows overlap. They are different because the species that may be oxidized and reduced in the electrolyte are controlled by the Lewis acidity of the

medium according to the equations shown above. The neutral composition has a window of 4.4V; an extraordinary number!

Unfortunately, it is virtually impossible to utilize the 4.4V window of a neutral melt, because the neutral composition cannot be maintained in practice. Most chemical or electrochemical processes will shift the melt away from neutrality, thus causing the window to shrink to a much smaller value.

Recently, we have found a way to buffer the room temperature molten salt electrolyte at exact Lewis neutrality. The method resulted from the chance observation that sodium chloride was insoluble in neutral or basic compositions of the MEIC- AlCl_3 melt, but was soluble to varying degree in acidic compositions. The explanation for this turns out to be quite simple, yet it has very useful consequences.

The chemical equations shown above relating the melt components and the species formed may be rewritten as a single equation:



The MEI^+ spectator ion has been deleted to simplify the equation. The equilibrium constant for this reaction is very low (about 10^{-17}), so the reaction proceeds completely from right to left as written. The reason NaCl is soluble in acidic melt is that the chloride from NaCl is completely consumed by the above reaction, thus converting the Al_2Cl_7^- to AlCl_4^- and putting Na^+ into solution.

The addition of NaCl to an acidic binary MEIC- AlCl_3 melt is not only a fast and easy way to attain the Lewis neutral composition, but such a melt in the presence of excess NaCl is also buffered at neutrality. We have done experiments where we chemically or electrochemically attempt to shift the melt acidic or basic, but within certain limits the melt remains neutral. The implication is that we may do useful electrochemistry in the neutral melt that takes advantage of the 4.4V

window without losing the wide window at the first sign of acid or base. The practical utility of this buffered neutral chloroaluminate molten salt will be in the area of power sources. In May 1990 the Air Force filed an application with the US Patent Office entitled "Method and Composition for Chloroaluminate Molten Salts Having a Wide Electrochemical Window" on behalf of two chemists at FJSRL.

The availability of an electrolyte with more than a four volt window, E^0 , combined with favorable physical properties, provides the prospect for truly impressive energy densities. To the uninitiated, 4.4V does not seem particularly extraordinary, but one should keep in mind that such an electrical potential translates to a very high free energy difference between reactants and products. It is worth presenting some elementary thermodynamics to appreciate this. The relationship between E^0 and free energy, ΔG^0 , is

$$\Delta G^0 = -nFE^0,$$

where n is the number of electrons transferred per mole of reactant and F is Faraday's constant. If we could make a battery using the full 4.4V window, then the free energy available would be 1.01×10^5 Joules/mole. For comparison, the heat of explosion of TNT is 1.15×10^6 Joules/mole.

The alkali metals (lithium, sodium, potassium, rubidium and cesium) are well known for their ability to store energy. In fact, lithium has the highest reducing potential of any ordinary material. This is the reason why lithium batteries have been so heavily studied as high energy primary battery cells over the last few years. Major problems with the lithium electrode include safety (they explode), poor cyclability (difficult to make a rechargeable cell), and reactivity with almost all electrolytes. The right electrolyte could solve most of these problems.

The ternary molten salt described earlier composed of MEIC-NaCl-AlCl₃ and similar materials are good prospects for secondary batteries having active metal electrodes. Assuming the electrodes are well behaved in the molten salt electrolyte, theoretical energy densities in the range of our goal of 500 W-hr/kg are possible. Ternary mixtures with the appropriate alkali metal chloride other than sodium (Na) would be required for cells employing lithium (Li) or potassium (K) electrodes. The table of calculated energy densities are for cells selected to demonstrate the potential for high energy density among those with alkali metal anodes (Li, Na, and K). The cathode (Cu(I) and Ag(I)) are almost arbitrarily chosen and most probably could be changed to a more energetic material in the future.

A number of new issues must be addressed concerning the neutral melts buffered with alkali metal chlorides. The behavior of the alkali metals themselves is also crucial to the success of the proposed batteries.

- Can the concept of neutral buffered chloroaluminate molten salts be extended to other alkali metal chlorides?
- What are the physical properties of these ternaries, if they exist?
- How do the alkali metals themselves behave chemically and electrochemically?
- What is an appropriate cathode and how does it behave?

These are all fundamental concerns, and are the topics of much of the research in the Electrochemistry Task at FJSRL now. Substantial progress has been made over the last year on some of these questions.

One of the first properties one wants to know of a prospective new electrolyte is its melting point. For a ternary system, such as MEIC-NaCl-AlCl₃, the phase diagram

Theoretical Battery Cells with Active Metal Anodes

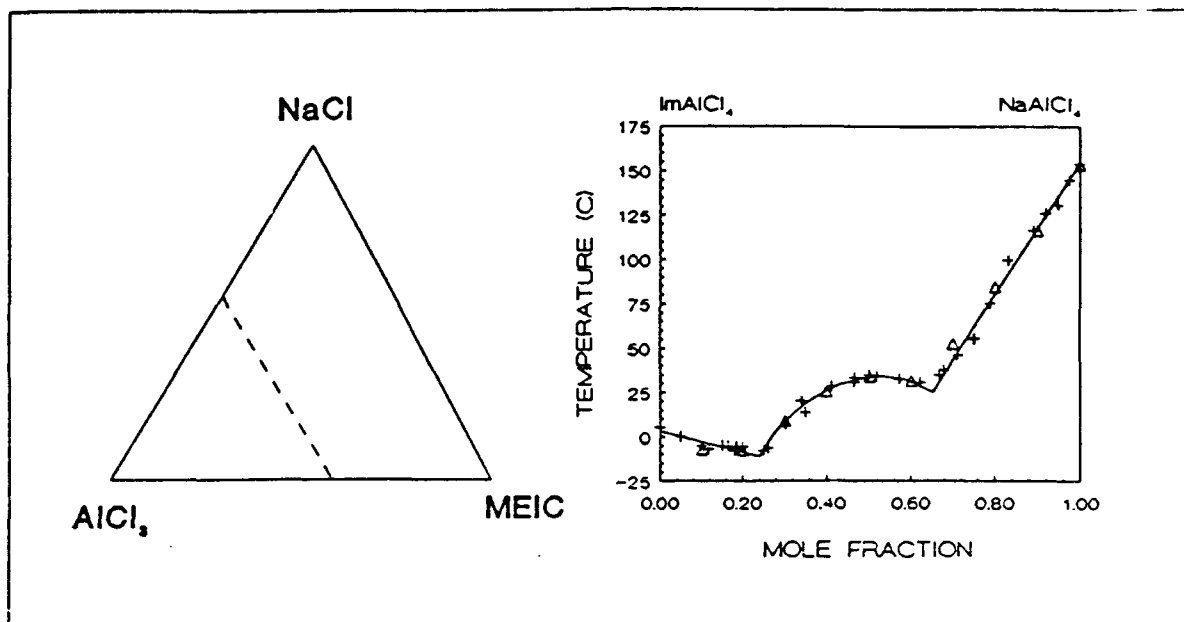
| Battery system | Calculated cell Voltage, V | Theo. energy density W-hr/kg |
|------------------|----------------------------------|------------------------------------|
| Lithium-Copper | 2.8 | 776 |
| Lithium-Silver | 2.8 | 506 |
| Sodium-Copper | 2.8 | 601 |
| Sodium-Silver | 2.8 | 458 |
| Potassium-Copper | 3.0 | 588 |
| Potassium-Silver | 3.1 | 455 |

is composed of the temperature contours located within the three axes of a triangular coordinate graph. Thus hundreds of painstaking measurements are necessary to assemble a complete ternary phase diagram. The most relevant part of the phase diagram of the MEIC-NaCl-AlCl₃ system was carefully measured by Mr. Jeffrey Boon at FJSRL. He realized that the Lewis neutral compositions would be the technologically important ones, and those were compositions traversing a line parallel to the NaCl-MEIC axis at a constant AlCl₃ mole fraction of 0.5. The problem then reduced to the relatively simple binary of two salts: MEIAlCl₄ and NaAlCl₄. That binary phase diagram shows two eutectic points and a syntectic point (*i.e.* two minima and a maximum). We were relieved to see that a wide range of compositions had melting points below room temperature. The determination of the complete ternary diagram awaits some student or technician brave enough to venture into the *terra incognita* of the Lewis acidic and basic territories.

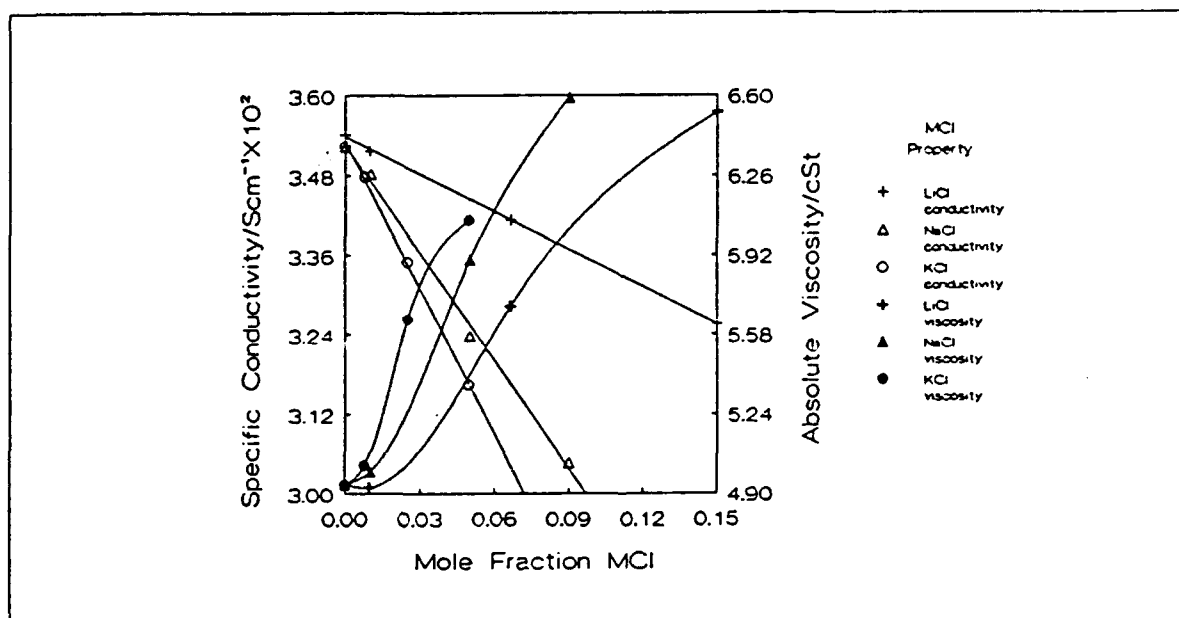
The phase diagram showed that it will at least be possible to work with the ternary sodium melts at ordinary temperature. One bonus expected of the ternary is the enhancement of electrical conductivity caused by the replacement of some of the large MEI⁺ cation with small spherical Na⁺ cation. This improvement, to a degree determined by the mole fraction NaCl in the melt, would be due to the more facile charge transport expected from the small Na⁺ relative to the lumbering MEI⁺.

Unfortunately, reality runs counter to expectations. Dr Anselmo Elias, a visiting professor at FJSRL, carefully measured the electrical conductivities, viscosities and densities of the MEIC-NaCl-AlCl₃ melts as a function of composition and temperature. The temperature dependencies are about as expected; that is the conductivity rises and the viscosity and density fall with increasing temperature. Surprisingly, as more sodium ion (Na⁺) replaces the large imidazolium ion, the conductivity goes down. At the same time, the viscosity increases with increasing Na⁺ content.

Our experience with the physical properties of the binary MEIC-AlCl₃ molten salts can help us explain the phenomenon. Earlier work at FJSRL showed that strong associations between the imidazolium cation and the chloride anion in basic compositions caused a decrease in conductivity and increase in viscosity. Dr Elias proposed a similar mechanism for the related behavior in the MEIC-NaCl-AlCl₃ ternary system. The association must include Na⁺ as one of the ions, since the properties change when the Na⁺ concentration is changed. It is unlikely that Na⁺ would interact significantly with the MEI⁺ due to like charges. That leaves a Na⁺...AlCl₄⁻ interaction of some sort to explain the changes in transport properties. The same transport properties in the analogous lithium, potassium, rubidium and cesium ternary systems behave similarly, except we found the melts containing KCl, Rb, or Cs to have a much lower solubility of the alkali metal halide.



Phase diagrams for the MEIC-NaCl-AlCl₃ Molten Salt. The ternary diagram on the left requires many melting point measurements to establish contours of phase equilibria. The dashed line defines compositions with a constant AlCl₃ mole fraction of 0.5. All compositions along that line are Lewis neutral, since the only anion is AlCl₄⁻. The binary diagram on the right shows the melting transitions for those neutral compositions of the MEIC-NaCl-AlCl₃.



Transport properties of MEIC-MCl-AlCl₃ ternary molten salts. M is the alkali metal Li, Na, or K. In all of the melts, the conductivity decreases and the viscosity increases as the MCl content is raised. We interpret these changes in terms of ion-ion associations in the ionic liquids. Rubidium and cesium chloride ternaries (not shown) are even more viscous and less conductive.

Dr. Elias noted that the syntectic point in the MEIC-NaCl-AlCl₃ phase diagram implied the presence of a single compound at that composition that could be crystallized and isolated. After many trials crystals of the composition MEINa(AlCl₄)₂ were isolated and an x-ray diffraction structure deciphered. That crystal structure clearly shows a network of AlCl₄⁻ anions held together by six-coordinate Na⁺ cations. Since all of the anions and half of the cations are tied up in this polymer-like structure, the reason for the lower conductivity is clear. The sodium ions, while in fact much smaller than the MEI⁺ ions, have their mobility severely constrained by the network of associations.

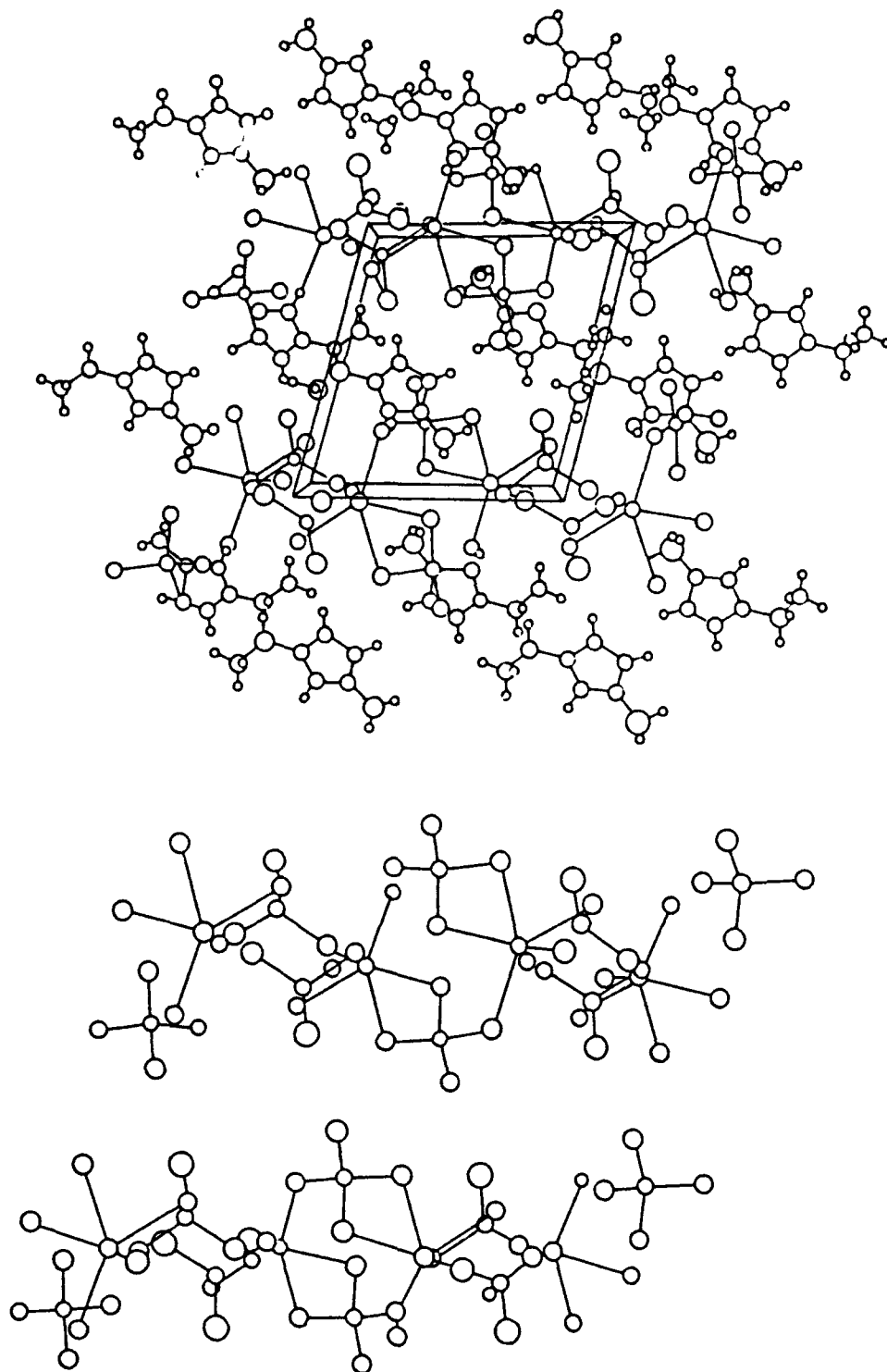
X-ray crystal structures are absolutely unambiguous for the relative positions of the ions in the salt. One must keep in mind, however, that we are really interested in the molten state; not the solid state structure. There are several arguments that can be made that the interactions in the solid are in general similar to the molten state, if not in detail. Nevertheless, we felt it important to attempt to find a method to directly examine the dynamics of the liquid state of the salt.

Another NRC fellow, Prof. W. Robert Carper, arrived while Prof. Elias was puzzling over the results of his transport properties measurements. Carper had extensive experience in the application of nuclear magnetic resonance (NMR) relaxation methods to the study of the dynamics of molecules in solution. The intensity of an NMR signal from a nucleus depends on the rate of relaxation from the inverted state to the ground state. There are many mechanisms for the relaxations, but if the simplest and most common mechanism pertains, then the relaxation rate may be interpreted in terms of the rate of tumbling of the molecule containing the nucleus under observation. The molecular (or ionic or atomic) tumbling rate is expressed as the correlation time (τ_c), which is the time required for rotation through one radian.

In the case of the MEIC-AlCl₃ binary and the MEIC-NaCl-AlCl₃ molten salts we chose to use the ¹³C nuclei in the MEI⁺ ions as the "observers" in the NMR relaxation technique. They would report to us the motion of the ions that contain them, and we know for sure that if the ion moves the carbon atoms inside it will move as well. The neutral compositions were chosen in order to reduce the number of different ions present; in this case AlCl₄⁻ would be the sole anion. Dr. Carper did all of the appropriate experiments to determine that the dominate relaxation was the one (it is called dipole-dipole relaxation) that may be simply interpreted in terms of correlation time. Arrhenius plots of these rates yielded the activation energy for the ionic motion, i.e. the energy barrier to rotation that must be overcome. The barriers for the carbons in the nitrogen-containing ring structure are about 5 kcal/mole, which is higher than expected for electrostatic interactions and about right for hydrogen-bonded interactions. Other spectroscopic studies from this lab in the past have shown hydrogen bonds linking chloride anions and the MEI⁺ cations at the ring positions. The NMR correlation times may be combined with the viscosity results we obtained earlier to yield the average radius of the tumbling moiety in the melts. That number, 10.6 Å, is much larger than the approximately 3.7 Å radius of the MEI⁺ model. The model of the ion was generated with the MOPAC modeling program developed by Dr. J. J. P. Stewart at FJSRL.

Our interpretation of this is that the MEI⁺ ion actually "drags" some of its counterions (AlCl₄⁻) with it as it rotates. Apparently it is easier to do this rather than break the relatively strong interaction that directly binds the anions and cations together.

If we could place an observer nucleus inside the cation, we could do the same for the AlCl₄⁻ anion. ²⁷Al is the naturally occurring isotope in greatest abundance, and it is NMR active. Unfortunately it is



Crystal structure of the MEIC-NaCl-AlCl₃ salt. The composition is a congruently melting material with the ions in ratios of $\text{MEI}^+:\text{Na}^+:\text{AlCl}_4^- = 1:1:2$. The top figure shows the packing of layers of MEI^+ ions interspersed with NaAlCl_4 layers. The structures of the MEI^+ have been deleted in the bottom figure to emphasize the $\text{Na}^+\cdots\text{AlCl}_4^-$ network.

a quadrupolar nucleus, with a spin of $5/2$. This complicates the interpretation of relaxation rates, due to the predominance of the quadrupolar relaxation mechanism in such a situation. Nevertheless, we determined the quadrupole coupling constants for ^{27}Al in three different binary and ternary melts, and then calculated correlation times. We were satisfied to see that the radius of the rotating species was the same 10.6\AA seen in the previous experiments. Another series of experiments with ^{23}Na as the relaxing nucleus (in the MEIC-NaCl-AlCl_3 melts of course) showed that all three ions have their motions correlated, indicative of the strong interactions binding them together.

The last few months have seen an increased emphasis on the study of the electrochemistry of active metals and their ions in the neutral ternary melts. Lithium and sodium are obvious first choices for this research, since we predicted very high energy densities for batteries employing them. We found out immediately that these metals are called "active" metals for

a reason. Impurities in the molten salts that were unimportant in all earlier studies suddenly were the cause of many problems due to the reaction between the metals and the impurities. In fact, it appears that under some conditions (perhaps most) the metals react with the melt components. Regardless, it is now clear that lithium and sodium can be deposited electrochemically from Li^+ or Na^+ in the ternary MEIC-LiCl-AlCl_3 or MEIC-NaCl-AlCl_3 melts. Whether we can devise a reversible lithium or sodium electrode or not awaits the results of experiments now in progress. The high reactivity of the materials make these the most difficult electrochemical studies we have undertaken to date. Of course, it is this very reactivity that we wish to harness for release in a battery cell, so we are well motivated to proceed. The goal of a very high energy battery is in sight, but there appears to be a rough road between our present state of understanding and our goal.